LARGE PLATE CdTe SYNTHESIS BY SEALED
VESSEL TRANSPORT

A. R. HILTON, PRINCIPAL INVESTIGATOR
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QUARTERLY TECHNICAL REPORT NO. 5

REPORT PERIOD: JANUARY 1 - MARCH 31, 1983

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20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

The fifth quarterly Technical Report for the program to grow large plates of high purity CdTe in a sealed system covers the period Jan. 1.- March 31, 1983. Last quarter, difficulties in applying the three zone growth process to 8" diameter plates were described. The major difficulty was plugging of the filters between the chambers. This quarter, the problem was solved by changing the order in which the elements were transferred. The process was used to prepare large grain plates four times in a row. Optical evaluation indicates high purity material. Evaluation as a substrate material is underway in other

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20. ABSTRACT (Continued)

laboratories. Next quarter, a 10" diameter plate will be prepared.

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SUMMARY

The goal of this program is to use vapor growth to form polycrystalline plates of cadmium telluride (CdTe) 6", 8" and 10" in diameter. The resultant material will be evaluated as substrates for mercury-cadmium-telluride (HgCdTe) growth and as an infrared optical material. Late in the program, mercury vapor will be used in an attempt to grow HgCdTe layers on the large area CdTe plates.

Previous workers have grown large plates of CdTe 6" in diameter transporting the vapor using an inert gas. The starting material was pre-compound. The method to be used in this program was to compound the material and transport the vapor through a filter into the casting chamber for growth in one operation under vacuum. Solid state recrystallization carried out at high temperatures over a long period of time will produce the desired large grain structure.

Results reported in the first three quarters demonstrated the initial process concept was impractical. Vapor transport of compounded CdTe in a sealed evacuated system was too unpredictable. High temperatures coupled with the presence of cadmium oxide caused a high percentage of quartz failures. Program goals could not be reached with the original process approach. The decision was made to convert to a three chamber quartz system in which the cadmium and tellurium vapors entered the plate chamber from separate tubes.

The new process approach was used ten times to produce 6" diameter plates from a stoichiometric melt. Plates weighing almost 2Kgms and possessing the required large grain structrue

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resulted. However, a void region was found to occur between
the faces of the plate each time. Growth from solution was
used to eliminate this problem. A plate was grown with grains
running from the bottom face to the top face from a solution of
approximately Cd45 Te55. Total process time was about 72 hours.

Application of the process to grow 8" diameter plates was
not successful at first. Plugging of the filters between the
chambers was the major problem. However, this quarter, the
problem was solved. The order of element transfer was changed.
Cadmium is transferred first into the round casting chamber.
The temperature is raised on both sides to trap the elements
in between in the round casting chamber. In this manner, the
solution concentration, grain size and growth conditions may
be controlled.

The process was used successfully four times in a row
to prepare 8" diameter plates weighing 1-3Kgms. The grains
were very large reaching perhaps 5-10 square inches and about
0.3-0.5" thick. Visual examination indicates the grains are
essentially free of precipitants. Measured infrared transmission
indicates high resistivity, high purity material because of the
lack of free carrier absorption. Attempts to further lower the
absorption coefficient by annealing material in cadmium and
tellurium vapor were unsuccessful.

Next quarter, evaluation results from other workers in the
HgCdTe field may become available Efforts to improve quality
will continue with the construction of a FLIR type lens. A
new three zone furnace will be placed in operation. The first
attempt to prepare a 10" diameter plate will carried out.

I INTRODUCTION

A crucial problem in the volume production of U. S. Government FLIR systems is the availability of mercury-cadmium-telluride (HgCdTe) detector arrays. Certainly fabrication of the arrays is difficult but the major problem is the availability of high quality detector material. The production of bulk HgCdTe alloy is a slow, difficult low yield process. The preferred method to produce detector materials is to grow HgCdTe layers epitaxially on a high quality cadmium telluride (CdTe) substrate. However, the availability of high quality Cd Te is also limited. Part of the reason for the shortage is that the conventional method for preparing CdTe crystals is to slowly (0.1"/hour) zone refine small diameter (1") crystals using the Stockbarger technique. The purpose of this program will be to develop an alternative approach.

Large plates of high purity large grain cadmium telluride will be grown from the vapor in a sealed system. Cadmium telluride will be compounded from the elements and sublimed through a filter into a separate growth chamber 6", 8" or 10" in diameter. Grain size will be increased by solid state recrystallization. Material thus produced will be evaluated regarding purity, optical homogeneity and suitability as substrates for HgCdTe growth. Attempts will be made to grow HgCdTe layers by mercury vapor deposited on large area plates insitu.

II. VAPOR GROWTH OF CADMIUM TELLURIDE

A. General

Cadmium telluride is formed from the group II element

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cadmium and the group VI element tellurium. All II-VI com-
pounds, as they are called, are difficult to grow because of
their high melting points and the fact that both constituent
elements are volatile. An appreciable vapor pressure exists
for each element at the solid melting point which leads to
complications for melt growth. For the same reason, vapor
growth of the solid becomes attractive.

Solid CdTe may be grown from the vapor at temperatures
considerably below its melting point, 1097°C, according to
the following equation:

$$Cd \ (g) + \tfrac{1}{2} \ Te_2(g) \ \rightleftharpoons \ CdTe \ (s)$$
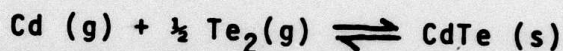
Where: g signifies gas or vapor
              s signifies solid

The reaction as written is reversible which indicates
that solid CdTe will sublime or vaporize into its constituent
elements. Thus, the source of Cd or Te_2 gas may be either the
pure heated elements or a heated source of pre-compounded CdTe
solid.

The quality of the CdTe grown from the vapor (or melt)
depends upon maintaining the exact ratio of 1:1 between the
cadmium and tellurium atoms. The pressure of cadmium vapor
(pCd) and the pressure of tellurium vapor (pTe_2) in equili-
brium over solid CdTe at the growth temperature is very cri-
tical and a function of temperature. Deviations from stoich-
iometry will occur if the ratios are not closely controlled.
Supplying the vapors from pure elemental sources heated sep-
arately and mixed together at the reaction sight is not too
accurate. Even the use of inert carrier gasses does not im-
prove the situation to any great extent. Sublimation of pre-
compounded CdTe followed by removal of the vapor to the reac-
tion sight is far more accurate. The compounded material may

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be weighed to an accuracy of 0.1% or better. The accuracy of the ratios may be maintained through direct sublimation in a closed system or through use of an inert carrier gas in a flowing system.

One quality criteria not mentioned thus far is crystallinity. In melt growth, crystals of one single grain may be grown provided that a seed is used and growth rates are very slow. Such restrictions are also the prime limitation relative to diameter of the crystal. In vapor growth, crystals are grown on other crystal surfaces of the same or similar structure, or they grow on an amorphous substrate with spontaneous nucleation and growth occuring over the entire surface. The first case may produce single crystals provided that growth conditions are carefully controlled. The latter method may produce large grain material provided high growth temperatures are maintained over long periods of time.

B. Previous Work

The first extensive investigation of the preparation of CdTe was carried out by D. de Nobel [1] of Phillips. The results published in 1959 details the thermodynamic properties, optical, electrical and semiconducting properties of the materials. The liquidus-solidus curve and related pressure-temperature studies have served as the basis for melt growth of CdTe over the years. Discussions related to melt growth will not be repeated here only as they are relative to vapor growth.

L. R. Shiozawa and co workers at Gould (now Cleveland Crystal Laboratories) carried out an extensive investigation

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beginning in the late 1960's concerning the vapor growth of II-VI compounds generally [2] and cadmium telluride [3] specifically. Diagrams from their papers will be used to discuss the problems involved in vapor growth of cadmium telluride.

Figure 1 shows the simple binary phase diagram of the Cd-Te system [2]. The diagram indicates a single compound is formed, CdTe, which has a congruent melting point of $1092^\circ C$. The term "congruent melting point" indicates that except at perfect stoichiometry, below the $1092^\circ C$ melting point, both Cd rich and Te rich liquids exist in equilibrium with pure CdTe. The point is better illustrated in the diagram [4] shown in figure 2. Only in a vary narrow range of stoichiometric ratios does the pure CdTe and its equilibrium vapor pressure exist. The range is less than one part per hundred thousand or 0.001 percent. Minimum vapor pressure at all temperature exist along this line. Equilibrium vapor pressure would be exactly in the right ratio. However, considering the accuracy required, it is more likely that the solid cadmium telluride would be either Cd rich or Te rich. Vapors above the solid would reflect this fact and be larger than those above exactly stoichiometric material.

The pressure of cadmium at the cadmium rich boundry stability field as a function of temperature [2] is shown in figure 3. The tellurium rich [2] is shown in figure 4. In both diagrams, the data is compared to the pressure for the pure element, P Cd (1) and P Te2 (1). For the low temperature, the measured values are very close to those for the pure liquid or close to those corrected according to RAOULT's Law. RAOULT'S law states the vapor pressure of a component is lowered by its atomic fraction in a liquid mixture:
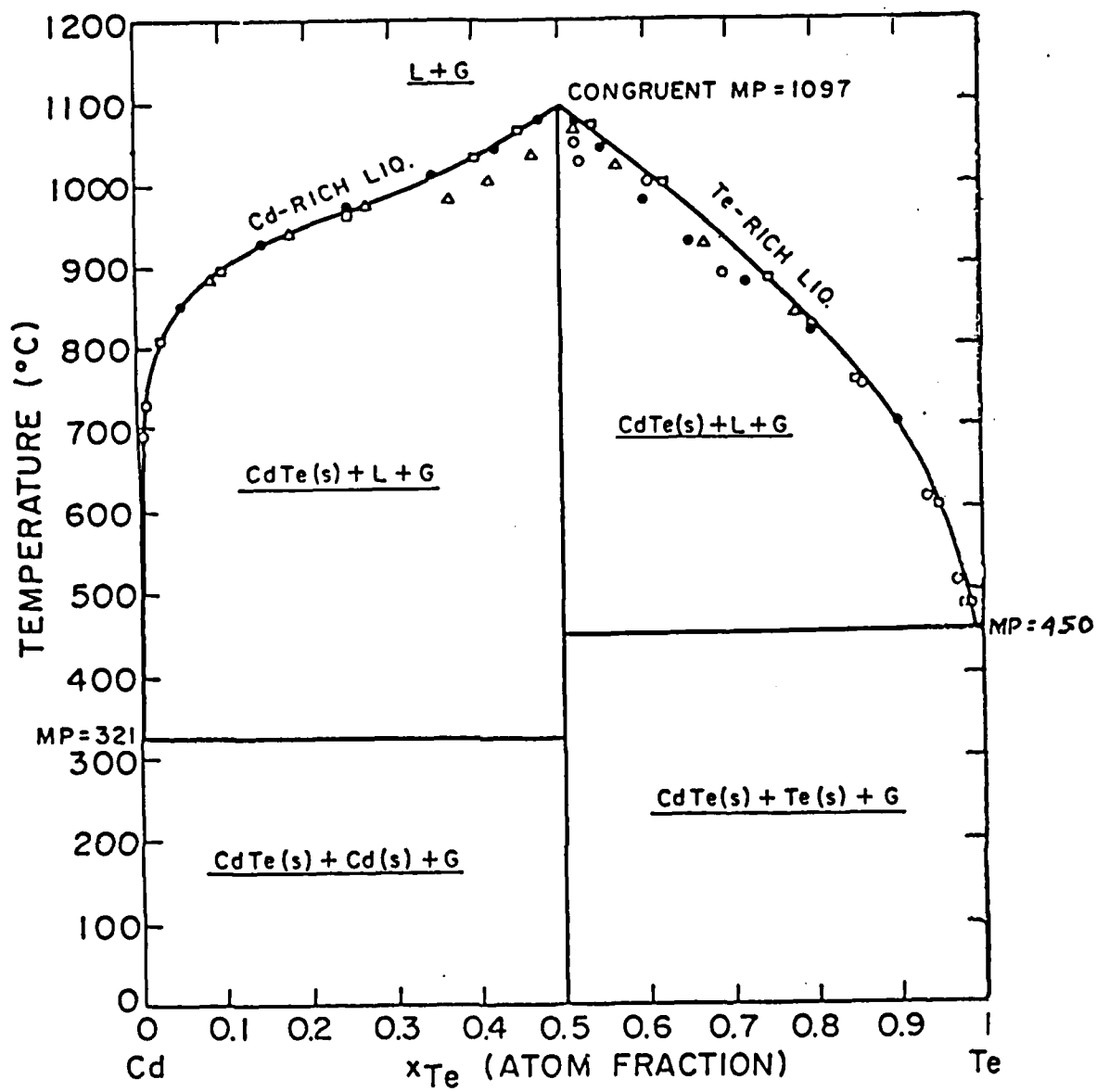
FIG. 1. PHASE DIAGRAM OF THE Cd-Te SYSTEM.
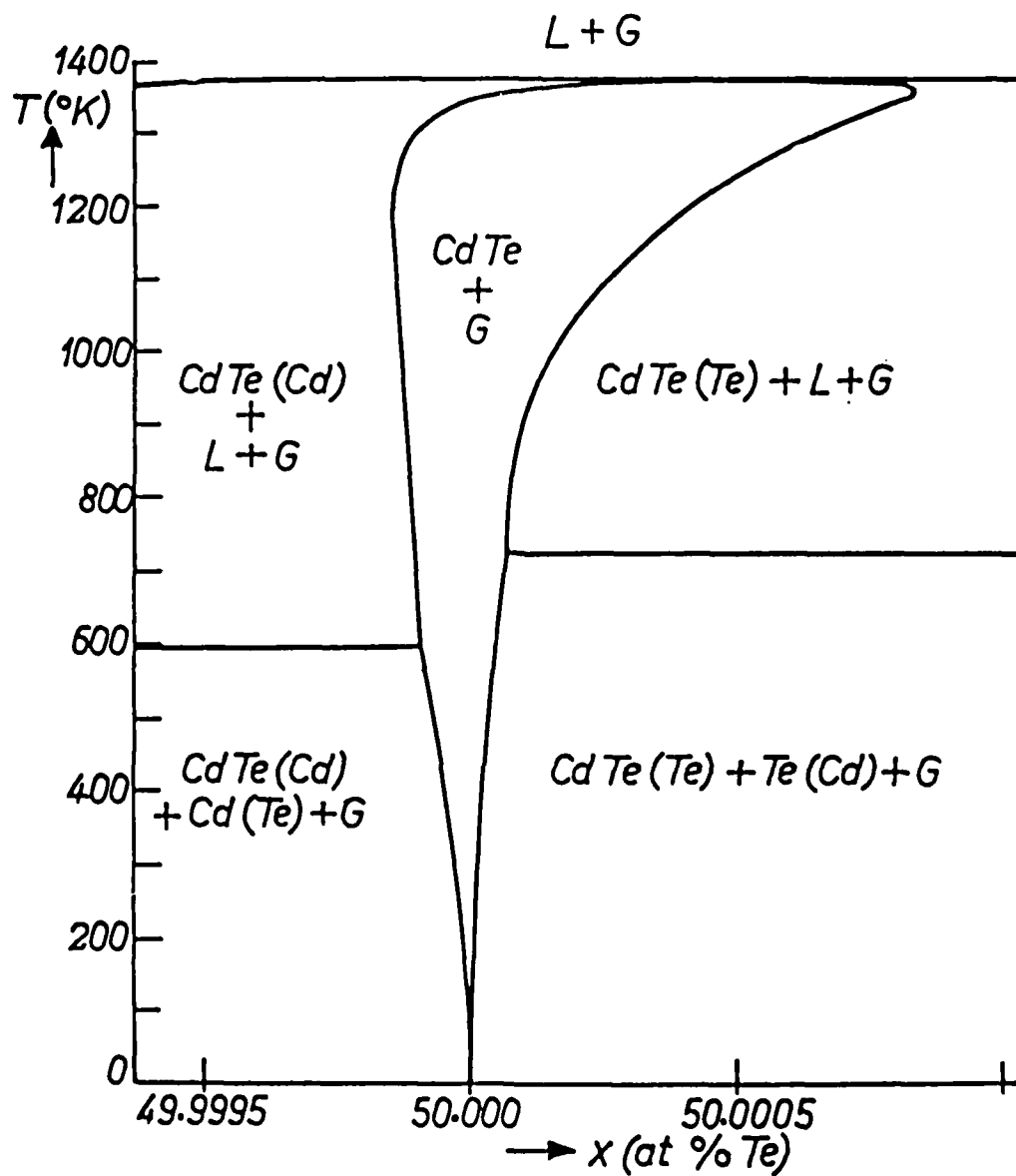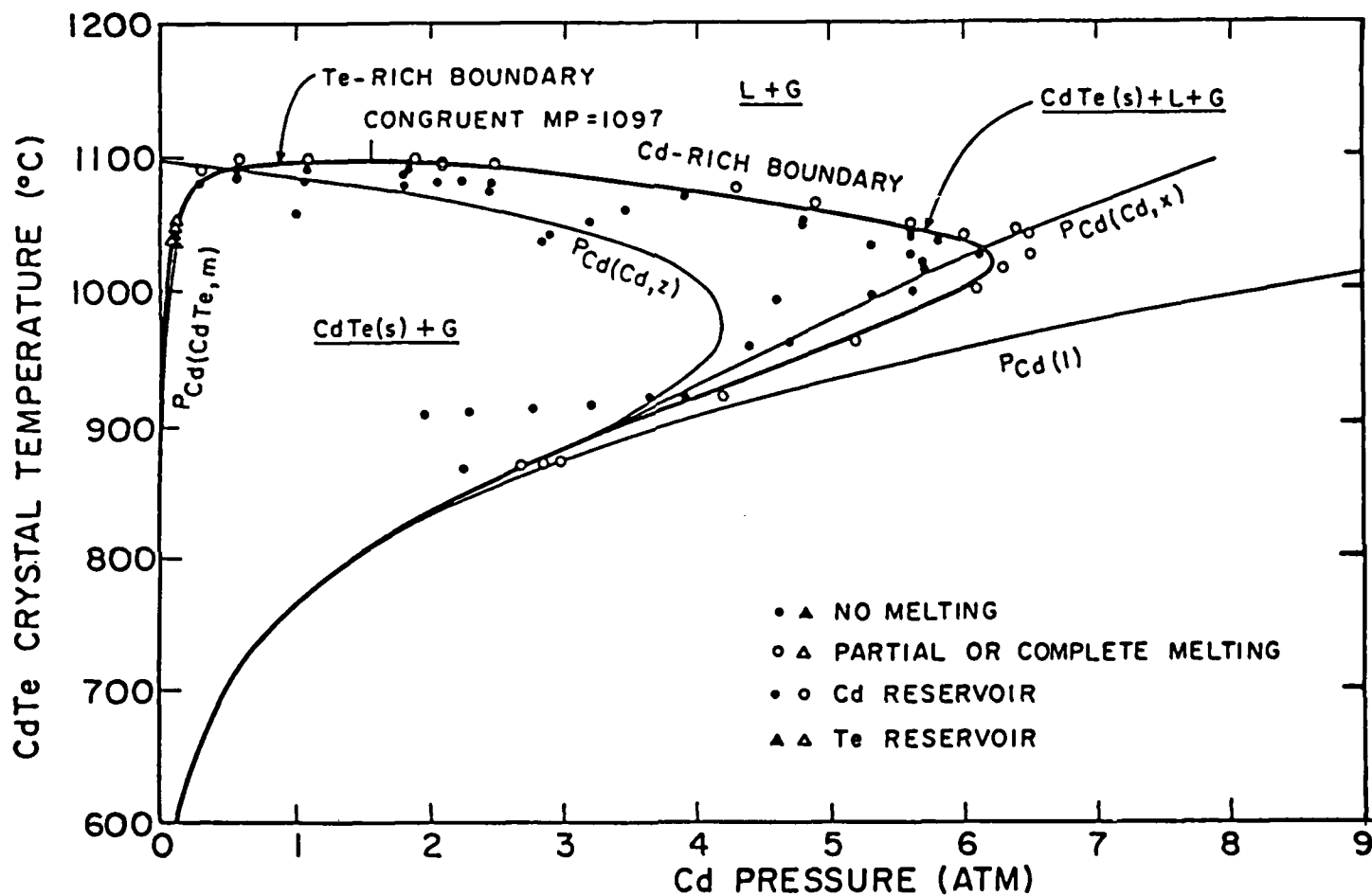
FIG. 2.   SOLID STABILITY FIELD OF CdTe.

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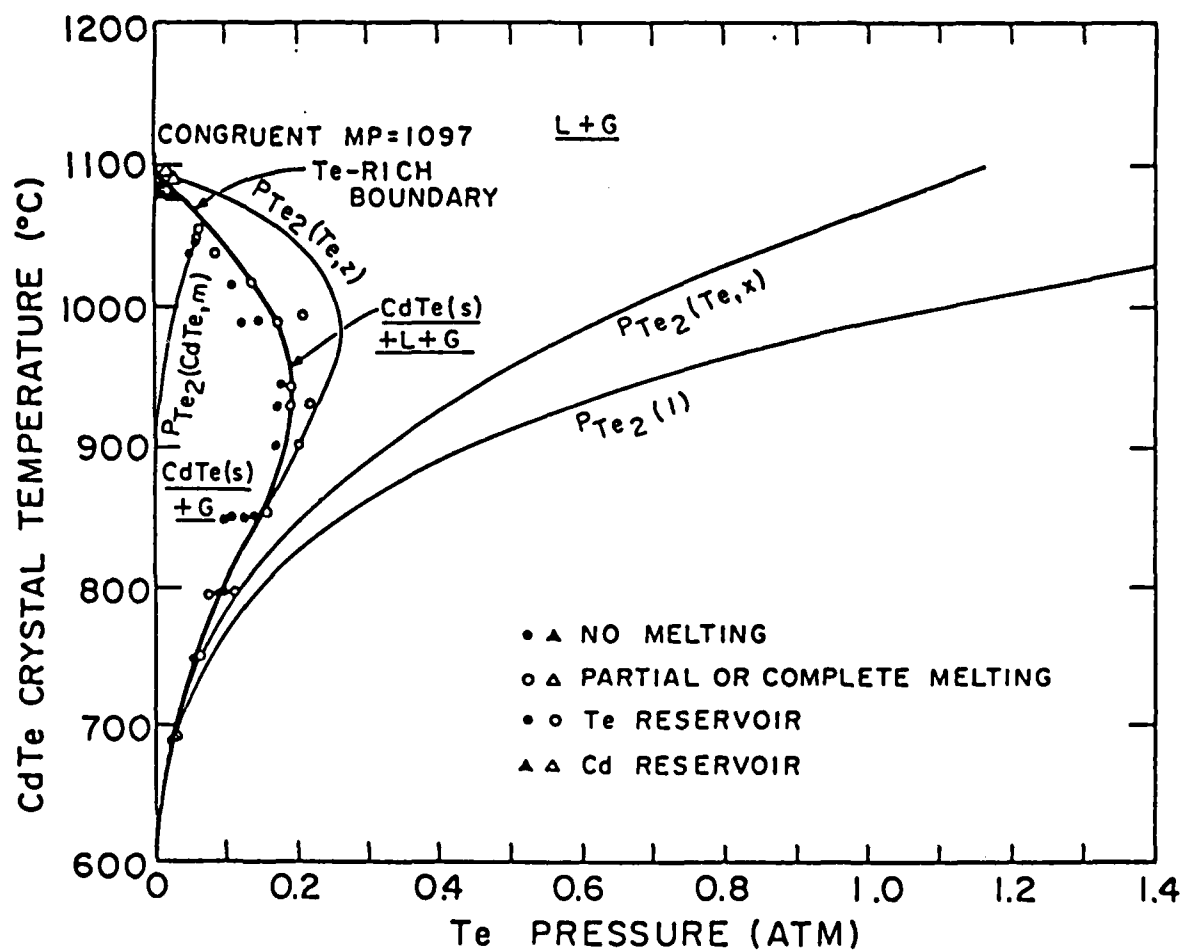FIG. 3. Cd-RICH BOUNDARY OF THE SOLID CdTe STABILITY FIELD. (PRESSURE-TEMPERATURE PROJECTION.)

FIG. 4. Te-RICH BOUNDARY OF THE SOLID CdTe STABILITY
FIELD. (PRESSURE-TEMPERATURE PROJECTION.)

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$$P\,Cd \quad = \quad x \quad P\,Cd\,(1)$$

Where   P Cd is the pressure of cadmium above
the melt

P Cd (1) is the pressure of pure cadmium
at the temperature of measurement

X   is the atomic fraction of cadmium in the
melt.

A similar statement may be made for the pressure of tellurium. The calculated curves using X are a simple application of RAOULT'S law. Those using the Z subscript indicates that association between the atoms in the liquid are taken into account. The curves labeled with the M subscript correspond to the minimum pressure conditions which exist with only pure Cd Te solid present.

The diagrams indicate that the pressure of cadmium may become very large, 4-6 atmospheres, around $1000\,^\circ C$ when compounding cadmium telluride. The pressure at the congruent melting point, $1092\,^\circ C$, is about 0.65 atmospheres. The vapor pressure of tellurium is quite low throughout the compounding range. The trick to compounding without an explosion is to stay close to the perfect stoichiometry point and allow time for the liquid phases to become small in quantity. The trick in vapor growth is to be sure that the subliming material is near the stoichiometric ratio so that the resulting vapors are close to the proper ratio. Maintenance of the proper ratio during vapor growth is complicated by the fact that tellurium exists as a diatomic gas, Te2. The effusion rate for a gas is inversly proportional to the square root of its molecular weight and directly proportional to its pressure. Therefore, for CdTe sublimation, we find the effusion ratios to be [2]

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$$R \ Cd/R \ Te_2 \quad = \quad (PCd/PTe_2) \quad (\ MW \ Te_2/MW \ Cd)^{\frac{1}{2}}$$

Where   R is effusion rate

P is pressure

MW is molecular weight

Even though the vapor starts out at the perfect 2/1 ratio, the cadmium atoms move faster changing the effusing gas mixture ratio. For Cd Te, the ratio becomes 1.33 instead of 2. Build up of the excess component may limit the deposition rate in a sealed system where equilibrium type conditions may be established. The equilibrium constant is given by:

$$K \ Cd \ Te(s) \quad = \quad (PCd) \ (P \ Te_2)^{\frac{1}{2}}$$

The build up of one component over the other shifts the equilibrium and suppresses further sublimation. Some have used capillary tubes to allow the excess component build up in the vicinity of the source to be pumped away or eliminated. Others have used a carrier gas to carry the subliming vapors, with perfect ratios, to the deposition surface.

C. Vapor Growth of CdTe Plates

Shiozawa [3] and co-workers at Gould used physical vapor deposition (PVD) to grow CdTe plates up to 6" in diameter. Figure 5 illustrates the type of systems used. Pre-compounded CdTe was sublimed from the hot zone of a furnace to a slightly cooler zone. Best results were obtained when growth temperatures of 1000-1050°C were used. Recrystallization was allowed to occur over periods up to 400 hours (17 days).

Figure 6 illustrates the type of grain sizes which were obtained. Growth and recrystallization at 950°C produced small grains. Fast deposition and short growth periods even at the high temperatures produced plates with samll grains and voids.

TEMPERATURE PROFILE OF FURNACE

~1060°C
~1040°C

TEMPERATURE PROFILE OF FURNACE

FURNACE

MULLITE ENCLOSURE TUBE

VACUUM ARGON CONNECTION

FUSED QUARTZ GROWTH TUBE

CARBON GETTER

CdTe SOURCE

FUSED QUARTZ GROWTH CUP
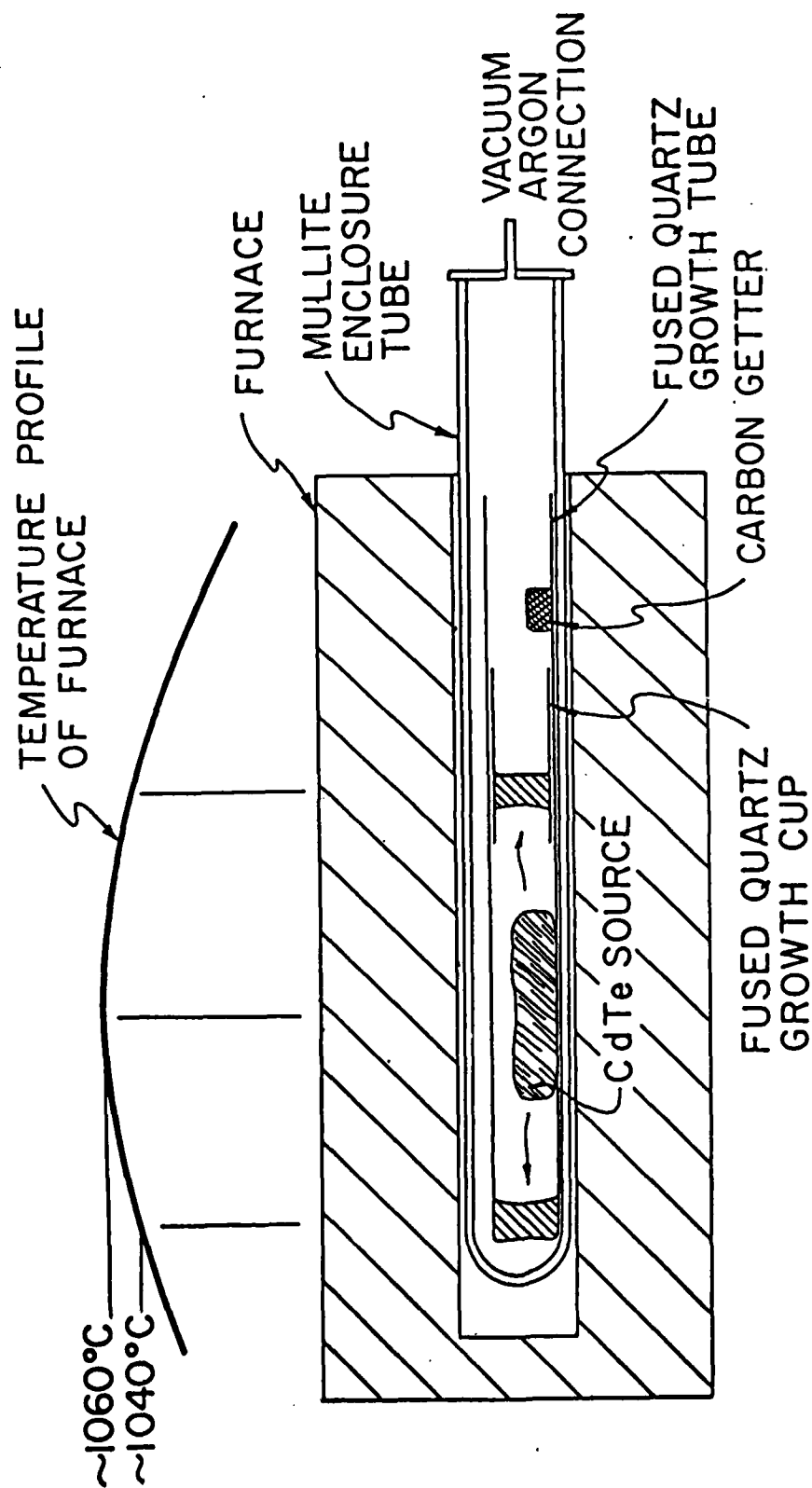
FIG. 5.   HORIZONTAL SYSTEM FOR CRYSTAL GROWTH BY GRAIN GROWTH

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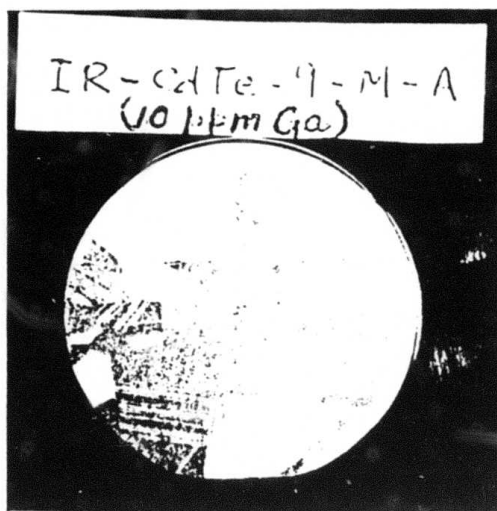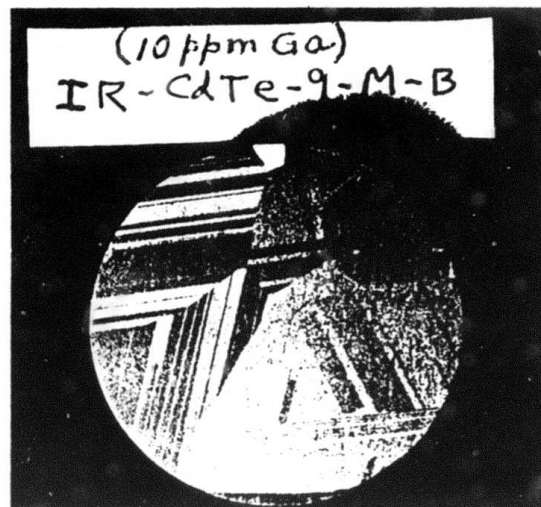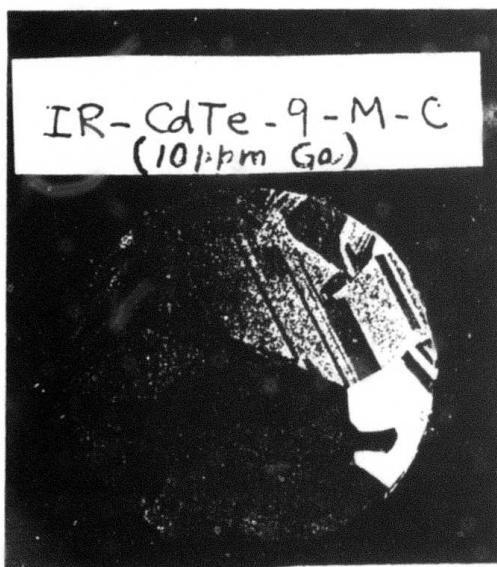
FIG. 6. Lapped Surfaces of CdTe Window Blanks Highlighting Grain and Twin Patterns.

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The systems were operated semi-sealed. Argon gas was used as a carrier. Pressures up to 1 atmosphere was used but 180 mm, the vapor pressure of stoichiometric Cd Te at 1050°C, was the preferred pressure. Later versions of the system used graphite parts to minimize the effects of air leaks. Also, inert gas was flowed through the furnace to protect the graphite components.

Plates thus produced were heat treated with both Te_2 and Cd vapors at temperatures of $700-800^{\circ}$C. Treatments were alternated and lasted 1-5 days. Measured absorption at 10.6μm was $0.001-0.002$ cm^{-1}. The effect of heat treating on the infrared transmission of one of their CdTe plates is shown in figure 7. From the transmission for Cd treatment alone, one can see that dual treatment is necessary. After treating with Te_2 vapor, almost theoretical transmission was obtained.
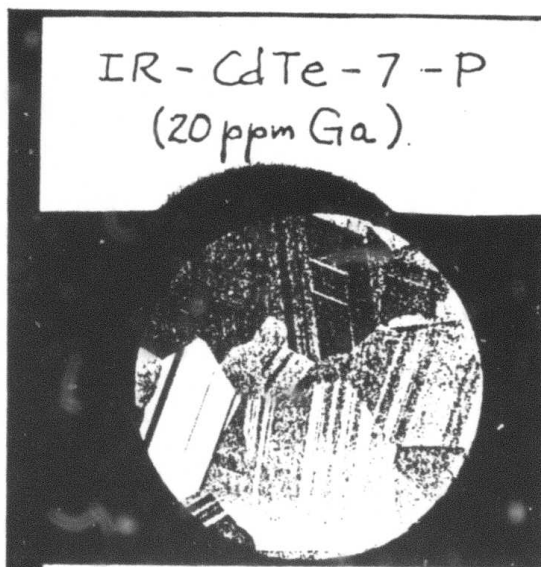
III APPLICATION OF THE AMTIR METHOD TO THE GROWTH OF CdTe

A. Preparation of AMTIR-1 glass

A simplified diagram depicting the glass compounding and casting process developed by Amorphous Materials, Inc. to produce AMTIR-1, is shown in figure 8. A high purity quartz container is placed in a dual zone resistive heated furnace. Zone 1 contains the round empty chamber which will serve later in the process as the casting mold. Zone 2 contains the glass compounding chamber. The process employed at Amorphous Materials combines all three glass processes (element purifications, compounding the glass and casting the plate) into a single continuous process.

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FIG. 7. OPTICAL TRANSMISSION OF Ga-DOPED CdTe
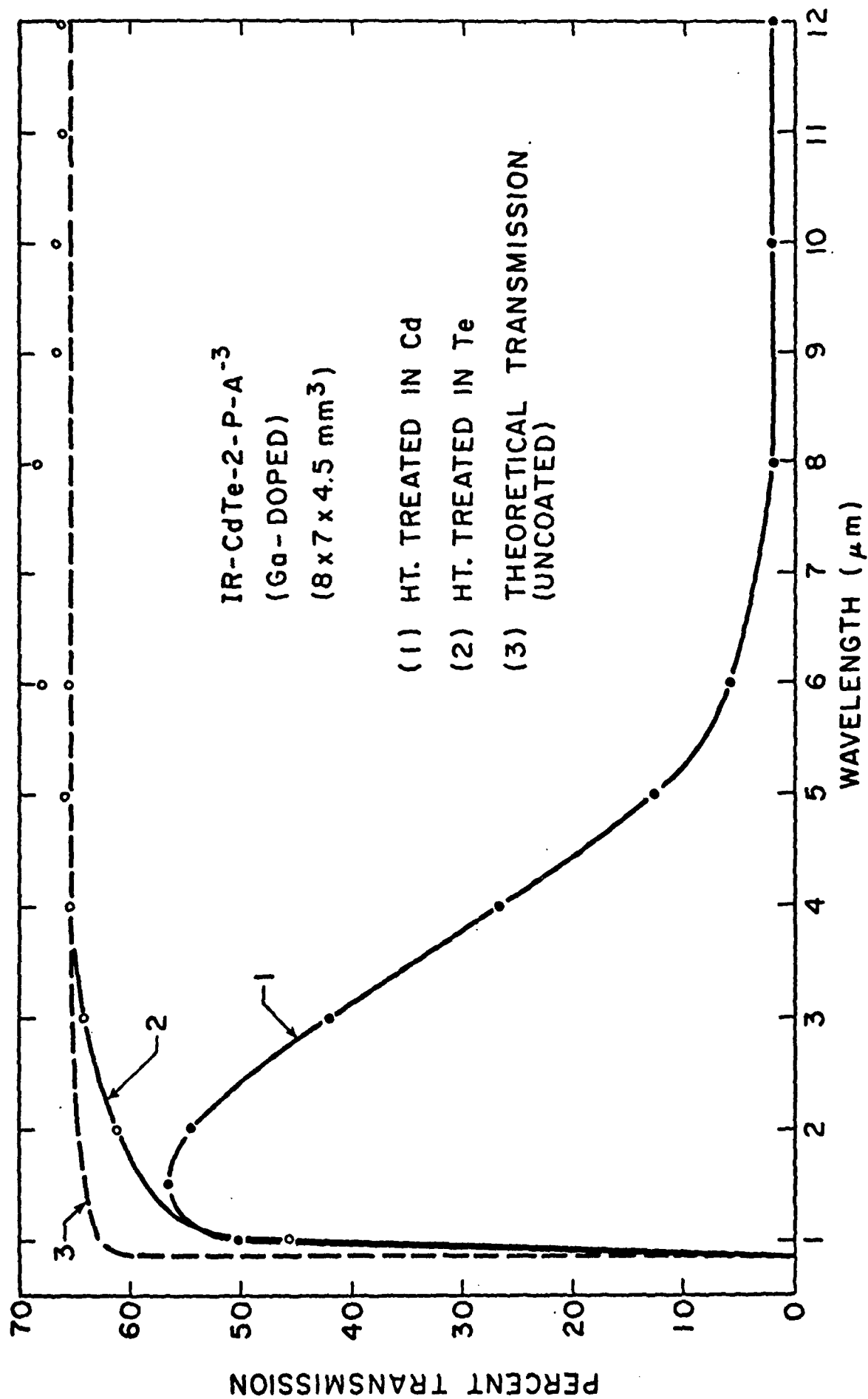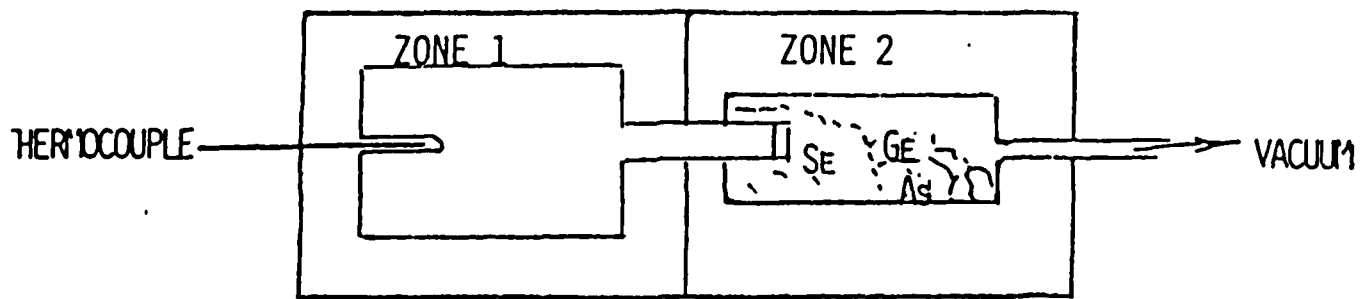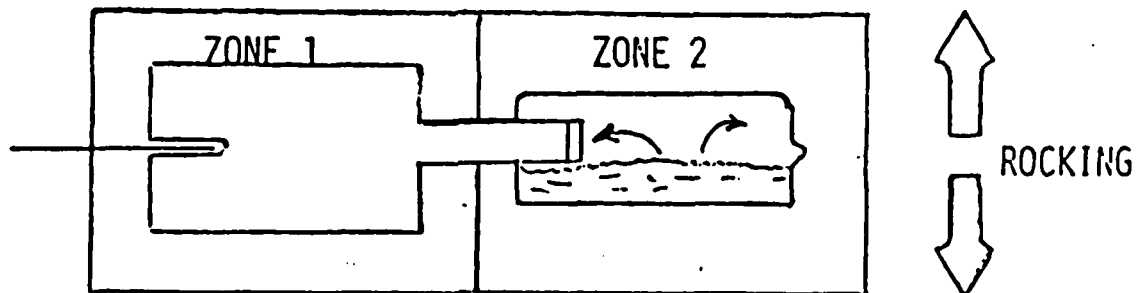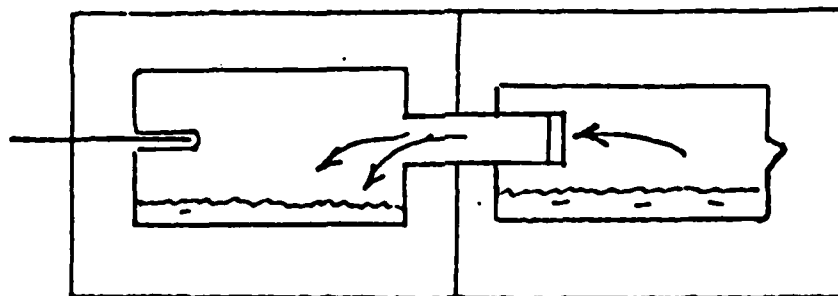
IR-CdTe-2-P-A-3
(Ga-DOPED)
(8 x 7 x 4.5 mm³)

(1) HT. TREATED IN Cd
(2) HT. TREATED IN Te
(3) THEORETICAL TRANSMISSION. (UNCOATED)

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FIGURE 8.   GLASS PROCESS DIAGRAM
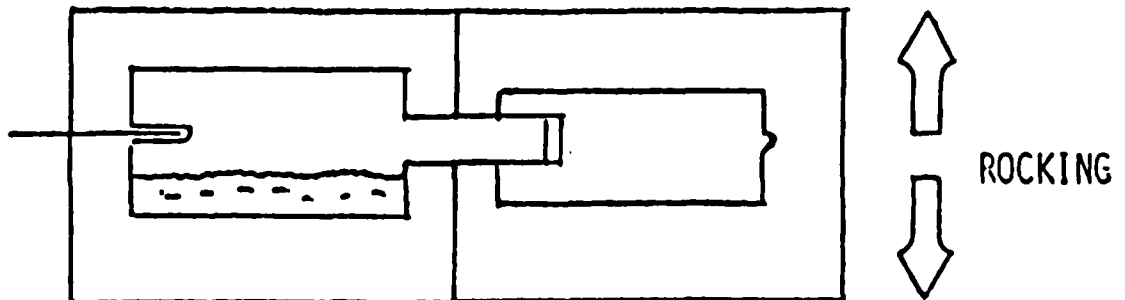

PURIFICATION

COMPOUNDING

DISTILLATION

CASTING

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In the first step, both chambers are evacuated and heated to remove moisture. A small amount of aluminum wire is added to the elements to act as a getter of oxides in the molten glass. After several hours, the chamber is sealed off while still under vacuum by heating and collapsing the pumping tube. The furnace is closed and need not be opened again until the glass is quenched.

The temperature is raised in both chambers while rocking the furnace. The casting chamber is heated to prevent premature transfer of the elements from the compounding chamber. The furnace is rocked for several hours to insure that all the elements have reacted properly and are uniformly mixed.

Rocking is stopped and the glass casting chamber cooled to allow transfer of the compounded glass into the casting chamber. Distillation occurs through a porous quartz filter which removes all particulate matter. The distillation generally takes 12-15 hours. The amount of material passed through the frit varies depending upon diameter and thickness. A 6" diameter plate 2" thick requires about 4Kgms of glass while a 8" diameter plate 2" thick requires 7Kgms of material. It is interesting to note that the purity of the finished material improves with quantity prepared. The total amount of impurities from quartz walls, vacuum system, etc. remains constant while the ending concentration decreases with increase in mass. The distilled glass is mixed by rocking. The glass is then allowed to cool while rocking down to the casting temperature range. Rocking is stopped and the furnace leveled up. The glass is rapidly cooled using compressed air to the anneal range $370^{\circ}C$. The glass is annealed 6-8 hours before being allowed to cool to room temperature.

AMTIR-1 glass is compounded in very unique and valuable high purity quartz containers. Casting chambers 6", 8" and 10" in diameter are routinely prepared. Methods have been worked out to open the chambers with a diamond saw so that the cast plate may be removed without breaking. The chambers are cleaned up and resealed for reuse. The compounding tubes are not saved. The impurities within the high purity beginning reactants are left behind during the distillation. The residues are sometimes quite large indicating the effectiveness of the method in preparing high purity solid materials.

B. Modification for Vapor Growth of Cd Te

The temperature range involved in cadmium telluride compounding and solid state recrystallization is 1050-1100°C, well above the compounding temperature used for AMTIR-1. However, the furnaces are of sufficient caliber to reach and maintain these temperatures continuously. Times involved are much longer. From start to finish the AMTIR-1 process requires 48 hours to produce a plate. High quality cadmium telluride grown from the vapor with solid state recrystallization (grain growth method) requires 300-400 hours (12-17 days) to produce good quality material 1" thick[3]. For a 6" diameter plate, 2700gms of cadmium telluride would be grown. Considering all these factors, the procedure carried out would be as follows:

1. The correct amounts of high purity cadmium and tellurium will be weighed out and placed in the compounding chamber as before. For a 6" plate, about 2700 grams will be required. High purity aluminum wire will be added (10-20ppm) to serve as an oxide getter. The casting chamber may need to be carbon coated using graphite formed from the pyrolysis of acetone.

2. The compounding and casting chambers will be heated to 200°C to remove moisture and the chamber will be tipped off.

3. The casting chamber will be heated to 1100°C. The compounding side will be heated to the boiling point of cadmium (765°C) and rocking begun. Over a period of hours, the temperature will be increased to 1100°C while rocking to insure complete compounding of the cadmium telluride.

4. Rocking will cease and material transfer begun. The casting chamber side will be reduced to a temperature of 1000-1050°C to bring about transfer of material to the plate side. The high temperature will be maintained so that grain growth will be a continuous process. Particulate matter and oxide impurities will remain behind in the compounding chamber. The time involved may be as long as 10-15 days.

5. After completion of the run, the cadmium telluride plate will be removed from the chamber using a horizontal glass saw as is done for AMTIR plates.

C. Program Objectives

A large diameter, thick, high purity, large grain plate of cadmium telluride will be formed. Individual large grains 1-4cm^3 in volume will be visible in the surface of the plate after lapping and light etching. Evaluation and treatment of the plate depends upon the desired use.

First emphasis of the program will be to establish the growth parameters using 6" diameter chambers. Purity of resultant material will be verified by chemical analysis. Electrical, mechanical and optical evaluation techniques will be

used where appropriate. After growth parameters are established, scale up for 8" diameter and 10" diameter plates will occur.

Substrates will be cut out of 6", 8" and 10" diameter plates for evaluation for HgCdTe epitaxial growth. Disks 2" in diameter and 0.1" thick will be prepared for evaluation by groups designated by DARPA.

Disks 2"D x 0.25" thick will be prepared for optical homogeneity verification. The disks will be polished flat and paralled in order to carry out MTF based image spoiling tests. Additionally, lenses will be fabricated for evaluation in the U. S. Army small imager FLIR common Module.

The last goal of the program will be to grow large area HgCdTe layers insitu. Mercury vapor will be admitted into the 6", 8" and 10" diameter CdTe growth chambers in an attempt to produce layer growth of the right composition.

D. Vapor Growth Results

The results obtained in 14 attempts to prepare CdTe plates using a stoichiometric vapor approach was discussed in detail in Technical Report No. 2. The major difficulties encountered are summarized below:

1. Numerous quartz failures occured probably due to the attack of cadmium vapor at high temperatures and moderate pressures.

2. Formation of solid CdTe in the filters caused plugging. The use of filters had to be abandoned early to aid attempts to transfer the stoichiometric material from the compounding chamber to plate chamber.

3. Sublimation of stoichiometric material in a vacuum system is difficult to control and unpredictable. Excess of one component relative to another will shift equilibrium conditons.

4. Deposition does not always occur where desired.

5. Analytical results reported in technical Report No. 3 did not demonstrate a purity improvement over the reactants. Filters were not used.

6. Trying to pass Cd and Te vapors through the same entrance at the same time to the plate chamber is the cause of major problems.

E. Vapor-Melt Growth Method

The conclusion reached from the vapor growth results
was that the Cd and Te vapors could not enter the plate
chamber through the same entrance. A three chamber zone
approach would be required if the program goals were to
be met. A diagram depicting the modification of the AMTIR
method is shown in figure 9.

The elements are melted and purified while being
pumped from both ends. After this step is completed and
the chambers sealed, one element is transferred into the
plate chamber and condensed as a liquid. In this case,
Te is transferred first. Condensation as a liquid in the
bottom of the chamber insures CdTe plate growth will occur
where it is most desired. Notice the plate chamber is wrapped
with quartz wool insulation to insure uniform temperature.

The second step involves compounding CdTe by transfer-
ring Cd vapor into the chamber. After the melt is compounded,
air may be blown on the bottom of the chamber to promote
crystal growth from the center and the bottom of the melt.
The procedure, equipment used and early results were reported
in Technical Report No. 3.

FIGURE 9.   THREE ZONE MELT GROWTH PROCESS

ZONE 1   ZONE 2   ZONE 3

VACUUM

CADMIUM
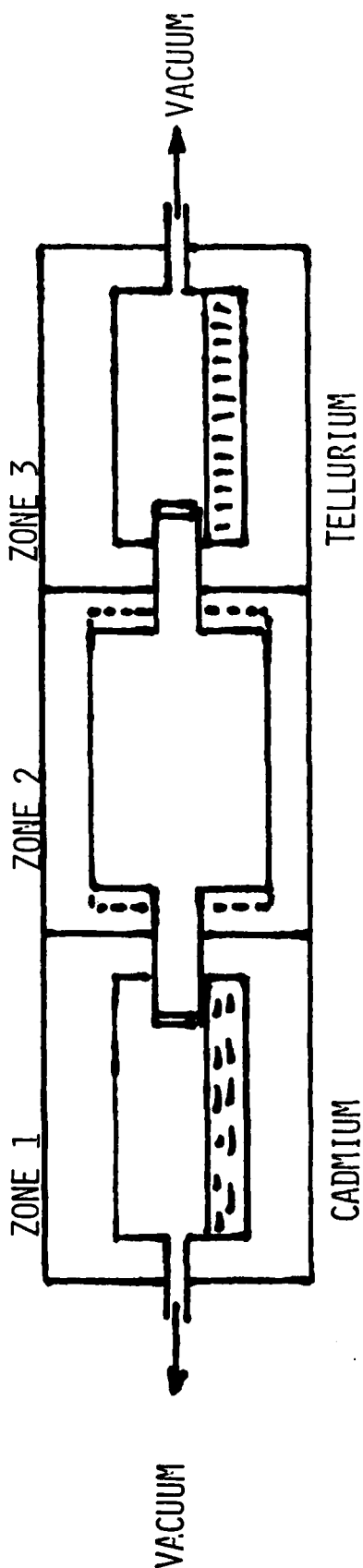
REACTANT PURIFICATION

TELLURIUM

TELLURIUM TRANSFER

INSULATION

AIR

CADMIUM TELLURIDE GROWTH

24
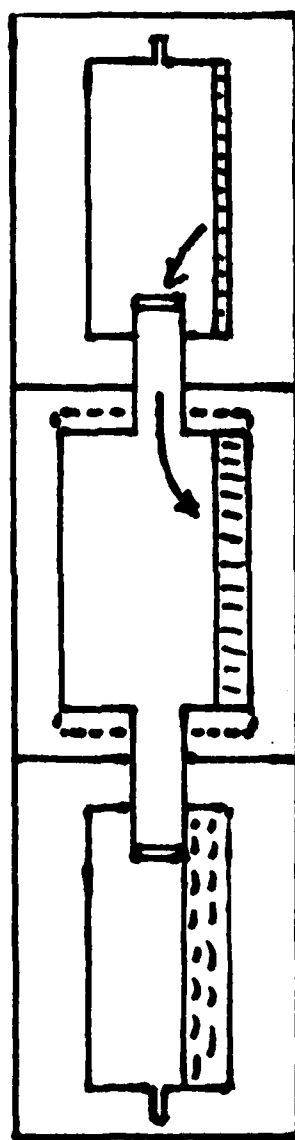
IV. Results for the Quarter

A. General

The conditions and results for all attempts to grow 8"
diameter plates using the three chamber solution growth process
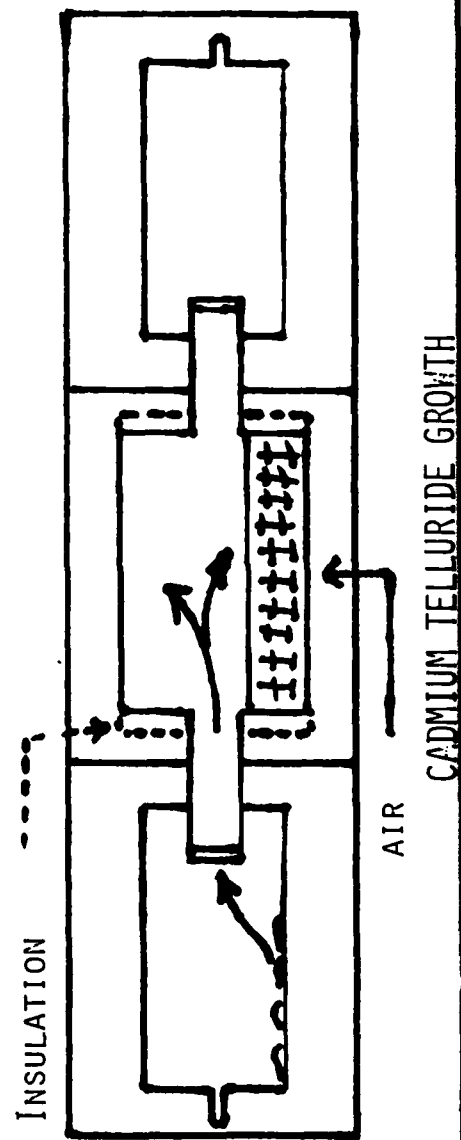are given in table 1. Only runs 32-40 occured in this quarter.
Results reported last quarter were essentially negative because
of failure to transfer the cadmium into the chamber containing
the tellurium. Plugging of the porous quartz filter was the
major problem.

Run No. 36 marked a departure from the procedures previously
followed. A quartz ball joint was used as a check valve to elim-
inate the premature mixing of the reactant gases which plugs the
filters. Unfortunately, the check valve became stuck. Attempts
to unstick the valve using cadmium pressure resulted in the ball
portion being blown through the quartz wall.

A carful study of all previous results made us realize
that the grain size would be determined by the composition of
the melt. The order of transfer of the elements had no effect
on the solution concentration. As long as all the pre-weighed
elements were transferred into the plate chamber, the solution
concentration (and thus the liquidus temperature) was determined.
We therefore decided to transfer the cadmium first and then in-
crease the temperature of both the tellurium and cadmium chambers
so the elements would be trapped in between. The plate chamber
could then be raised in temperature, slowly cooled with air blown
on the bottom on the center to initiate growth.

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TABLE 1. THREE CHAMBER MELT GROWTH RESULTS

RUN NO.	TYPE	SIZE	CONDITIONS	RESULTS
26	Solution	2Kgm.6"	45Cd-55Te,1090-800 Air 24Hrs.	Lg.Grain, 1 layer
27	"	6Kgm.8"		Cd Did not Transf.
28	"	" "	" "	" " "
29	"	4Kgm.8"	45Cd-55Te,1090-800, 24Hrs. Air	Most of Cd did not transfer
30	"	2.5Kgms.8"	Cd45 Te55, 1050-800, 24Hrs. Air, Cd transferred first	Small grain plate 0.3" Thick
31	"	2.5Kgms.8"	Cd45 Te55, 1050-800, 24Hrs. Tellurium transferred while Cd cooled	Most of Cd did not transfer, thin plate
32	"	2.5Kgms.8"	Cd45 Te55, 1075-800 Air,	Thin plate, most Cd did not transfer
33	"	2.5Kgms.8"	Cd45 Te55, 1075-800	Cd did not tranfer, poor quality
34	"	" "	Cd45 Te55, 1075-800 Air,	Small grain, thin plate
35	"	" "	Cd45 Te55, 1075-800	Cd did not transfer
36	"	" "	Cd transferred first, used check valve	Quartz failed
37	"	" "	Cd transferred first 1085/cooled, 6°C/HR	Good plate
38	"	" "	Same	Excellent plate
39	"	" "	Cd48 Te52, 1095, 3°C/HR	Good plate
40	"	3.3Kmgs.8"	Cd42 Te58, 1050, 3°C/HR	Good plate

B. Plate Results

Transfer of the cadmium first under the new conditions was tried first in run 37. The composition of the solution was Cd45 Te55. The solution temperature was raised to 1085°C and then slowly cooled at a rate of 6°C/HR. Air was blown on the bottom of the chamber. The procedure was very successful.

The plate removed from the chamber weighed over 2Kgms. However, tellurium rich solution and dendritic growth was found on the top. The plate was waxed to a piece of glass and the unwanted portion ground away revealing a large grain plate of cadmium telluride. A photograph of the resulting grain structure is shown in figure 10. Two views are given to show up grains by a different direction of illumination. Notice a small region of dendritic, porous material occurs on one edge.

Examination of the photograph reveals a grain which reached completely across the plate, 8"x½-1" in area. Large portions are single with some poly lines evident. All in all, about 1Kgm of useful material was made.

The same exact conditions were repeated in run 38 to demonstrate the results were reproducible. A photograph of the plate is shown in figure 11. The plate was inadvertently ground too thin in an attempt to completely eliminate the dendritic portion. As a result, the pressure of the diamond broke the plate, However, the nature of the grain structure can be seen. The results were excellent. Two grains are fully 5-6" long by 1-1½" wide. Large portions of the plate appear single. Most of the plate is made up of perhaps 5 regions of different orientation.
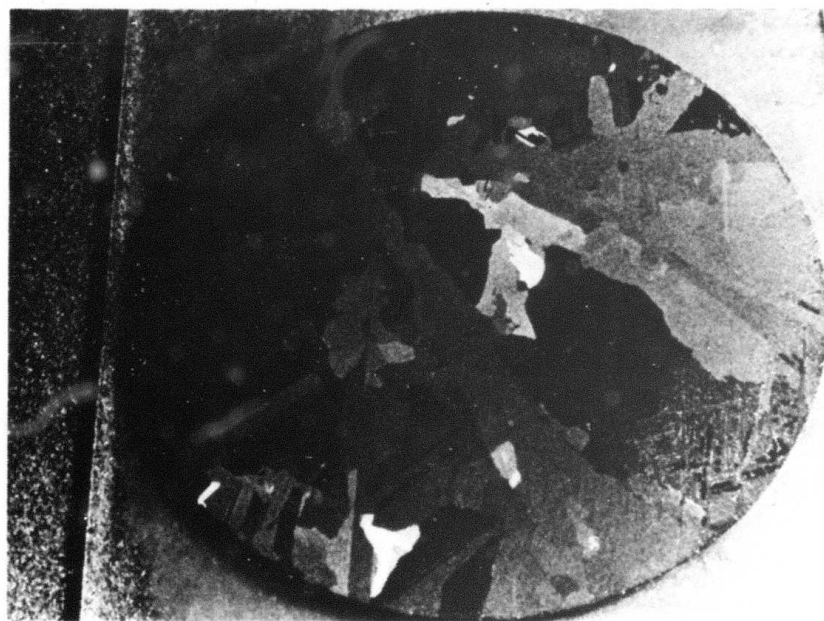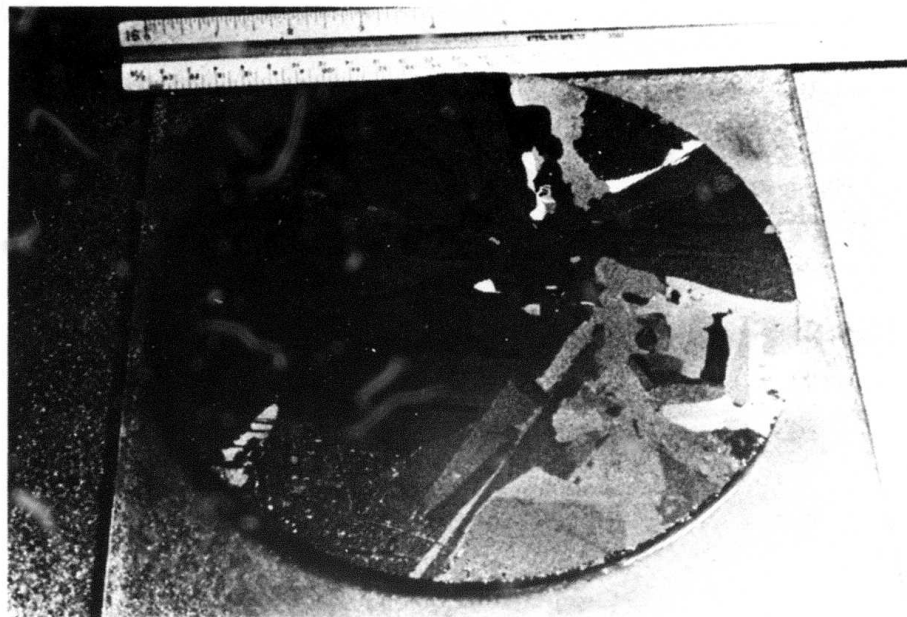
Figure 10 Photographs showing the grain structure of the
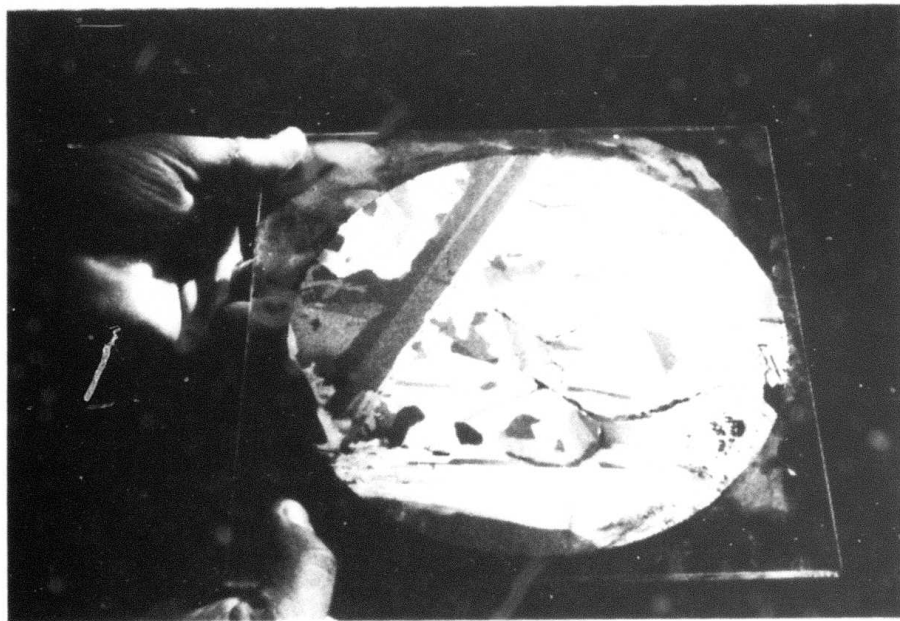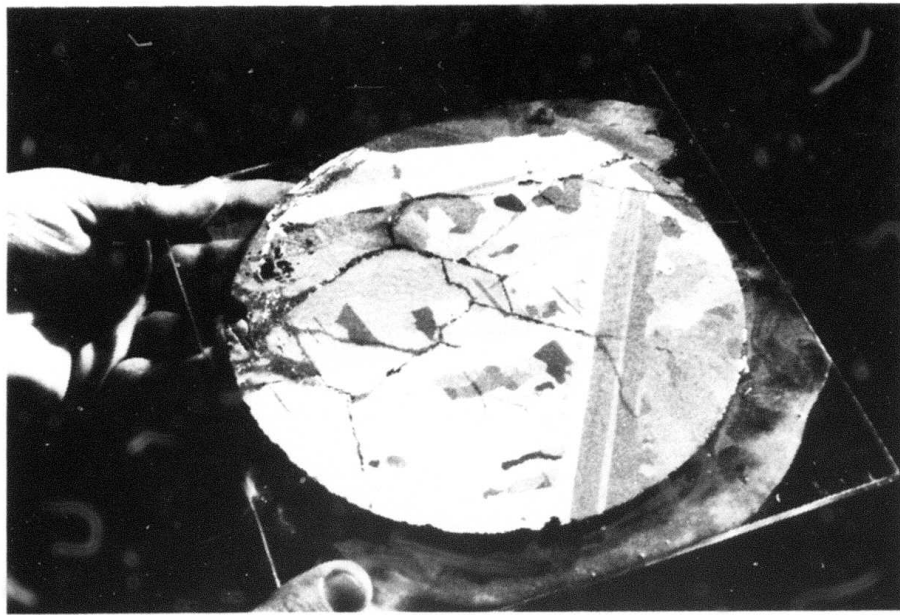8" plate from run 37.

Figure 11 Photographs showing the grain sturcture of the 8" plate from run 38.

The decision was reached to attempt to increase the regions of single crystal in volume even further by changing the solution concentration and the rate of cooling. Moving closer to stoichiometry would provide a higher liquidus temperature. A concentration of Cd48 Te52 was chosen. The rate of cooling was decreased from 6°C to 3°C per hour to promote slower growth. The resulting plate weighed 2.8Kgms when removed from the furnace. Grinding brought the weight down to 1.7Kgms or about a 60% yield. A photograph of the plate is shown in figure 12. Both top and bottom side photographs are shown. Note that some of the grains can be seen in both photographs demonstrating they have grown from the bottom through the plate. The overall quality of the plate was not as good as that of run 38.

The decision was reached to decrease the cadmium concentration and grow from solution at a slightly lower temperature. The concentration selected for run 40 was Cd42 Te58. A charge of 3.3Kgms was used. The growth temperature was 1050°C. When the plate was removed from the chamber, it weighed about 3Kgms. After grinding, the plate was 0.25" (6mm) and weighed about 1.2Kgms. The grain structure was good but somewhat smaller than runs 37-39.

C. Optical Evaluation

The plate from run 37 was left intact to serve as a demonstration of our ability to form 8" diameter plates. For this reason, samples were not prepared for optical evaluation.

Plate 38 was prepared in an almost identical manner. Samples were cut from this plate and polished for evaluation. The results are listed in table 2. Over the wavelength range

Top Side
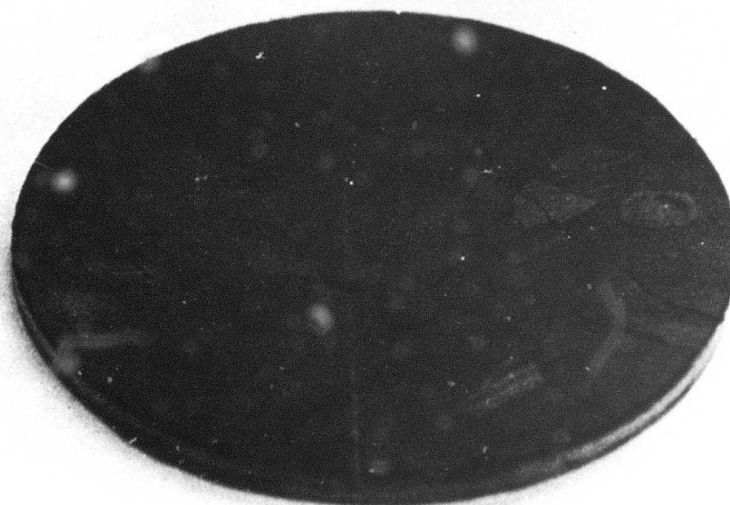
Bottom Side

Figure 12 Photographs showing the grain structure of the 8" plate from run 39.

TABLE 2. OPTICAL EVALUATION OF VAPOR-MELT GROWN CdTe PLATES

RUN NO.	% TRANS. 2.5-25um	THICKNESS cm	ABS. Coef.cm^{-1}	FREE CARRIER ABS.
38	58	0.4	0.17	none
39	50	0.8	0.33	slight
39 (Cd Vap.)	45-5	0.8	0.46-3.2	Yes, strong
39 (Te Vap.)	43-4	0.8	0.52-3.5	Yes, strong
40	50	0.6	0.43	none

2.5-25μm, free carrier absorption was not observed. The cal-
culated obsorption coefficient, $0.17cm^{-1}$, is about as good as
we have achieved thus far in either vapor or melt growth. How-
ever, examination with an infrared microscope indicated the
value should have been lower. The precipitates within the grain
were no longer readily apparent. Precipitation at the edge of
the grain or solution entrapment between grains produces dark
lines. Within the grains, the cadmium telluride appears much
cleaner.

Plate 39 was grown at a higher temperature and closer to
stoichiometry. One might reasonably assume that the absorption
within the material might be less due to less tendency to form
precipitants. Results shown in table 2 indicate this was not
the case. The calculated absorption coefficient was twice as
high as the previous plate. Pieces were cut from the plate
and heat treated in 0.2 atm. of cadmium vapor at 800°C for 12
hours. Previous workers at Gould [2] had used this method to
lower absorption. However, our results were just the opposite.
As indicated in table 2, free carrier absorption became very
strong. To correct the situation, we decided to vapor anneal
using tellurium vapor. We chose the conditions used effectively
previously [2] of saturated vapor (3×10^{-2} atm) at 700°C for
120 hours. Results presented in table 2 show that no improve-
ment was realized. Obviously, our anneal cycles will be diff-
erent from those used by previous workers to treat vapor growth
material.

Samples cut from plate 40 did not give as good results as
those from 38. Again, the absorption (or loss) was quite large.
The material was grown from a solution higher in tellurium con-
centration. It is not known at this time if the variation is
is related to solution concentration or to experimental varia-
tion between runs. Our obility to polish the material is poor

at this point which tends to complicate interpetation of our results.

D. Discussion of Results

The plugging problem has been solved. Solution of this problem qurantees we can control the solution composition accurately through precise weighing of the ingredients. We can now begin to control the growth process so that quality may be maximized for application. The only failures we can now expect are equipment in origin such as quartz breakage, thermocouple or controller malfunction. Everytime we start a run now, we get a plate. The same remarks may be expected to hold later on when we attempt 10" diameter plates.

Grain sizes produced are large enough to indicate a practical substrate source process may be developed. Growth of plates 8" in diameter with useful thickness of 0.5" seems possible. Such a plate represents 2Kgms or more of useful material grown in a relatively short period of time, 3 days. The true potential may not be assessed until information is received regarding the evaluation of samples in a conventional liquid phase epitaxial mercury-cadmium telluride growth process. The potential regarding vapor phase growth may be different because substrate orientation may not be a factor. At this time, the large area of our plates offers a definite advantage to those interested in vapor phase growth.

The physical strength of small grain plates may be needed for optical applications. Fabrication of cadmium telluride is very difficult requiring unusual skills like those developed at II-VI Corporation. Optical quality material will be grown from solutions more dilute in cadmium concentration then those

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for substrates. The resulting lower liquidus temperature
will lead to smaller grains. The process will be developed
separately.

E. Outside Evaluation

A number of rectangular samples were cut from plate 38
to be used for evaluation by other organizations. Samples
were provided to Dr. Castro of Texas Instruments Central Research
Laboratory. Solution epitaxy growth will be attempted. Large
area samples were provided to Dr. Kay and Dr. Roschen of Ford
Aerospace for evaluation using vapor growth methods. Physical
characterization of samples will be provided by Dr. Evans of
Charles Evans & Associates. Very large samples from plate 40
were sent to Dr. Poppendiek of Geosciences Ltd. for measurement
of certain physical parameters. Copies of report No. 4 were
also sent to several people who have active mercury cadmium
telluride programs.

No anlytical results were available for these plates.
The delays in obtaining emission spectagraphic results were
excessive. A new source of data will be found.

V. Plans for Next Quarter

1. The image spoiling test will be performed on different regions of the same plate. A similar procedure was used during the AMTIR-I MM&T program to verify optical homogeneity.

2. A FLIR type lens will be fabricated from the polished plate evaluated for homogeneity. The lens will be plano/convex to take advantage of the already generated flat surface. The Diversified Optics MTF test station will be used to evaluate the individual lens element.

3. A new three zone furnace was ordered and will be put in service hopefully to improve the quality of the material.

4. Quartz required for 10" diameter plates has been ordered. First attempt for 10" plates should occur this quarter.

5. Effort will be expanded in developing a method to generate substrates from the large grains of the 8" plates.

6. Efforts will continue to improve the quality of the material produced.

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